

# **Elements of Quality Assurance in Monitoring Volatile Organic Compounds at Trace Levels**

by

**W. McClenny**

**NERL, USEPA, RTP, NC;**

# Objective

To Identify Critical Factors in Obtaining Accurate VOC Data with Diffusive Sampling.

# Subjects Covered

- **Diffusive Sampling Badge Design and System Components.**
- **Ease of Use - Any QA Tradeoffs?**
- **Choice of Adsorbents – How to Estimate Adsorbent Capacity?**
- **Ideal and Non-Ideal Compound, Adsorbent Combinations.**

# Subjects Covered (Cont.)

- Lot-to-Lot Variability of Adsorbent/Sampler Combinations
- Testing for Different Environments
- Consistency Checks

# Diffusive Sampling Badge Design and System Components

- The Tube-type Diffusive Sampler
- Sampler Storage Accessories
- The Thermal Desorber
- The GC/MS System
- Calibration Gear
  - Exposure Chamber
  - Target Compounds in Compressed Gas Cylinders
  - Certified Flow Controllers

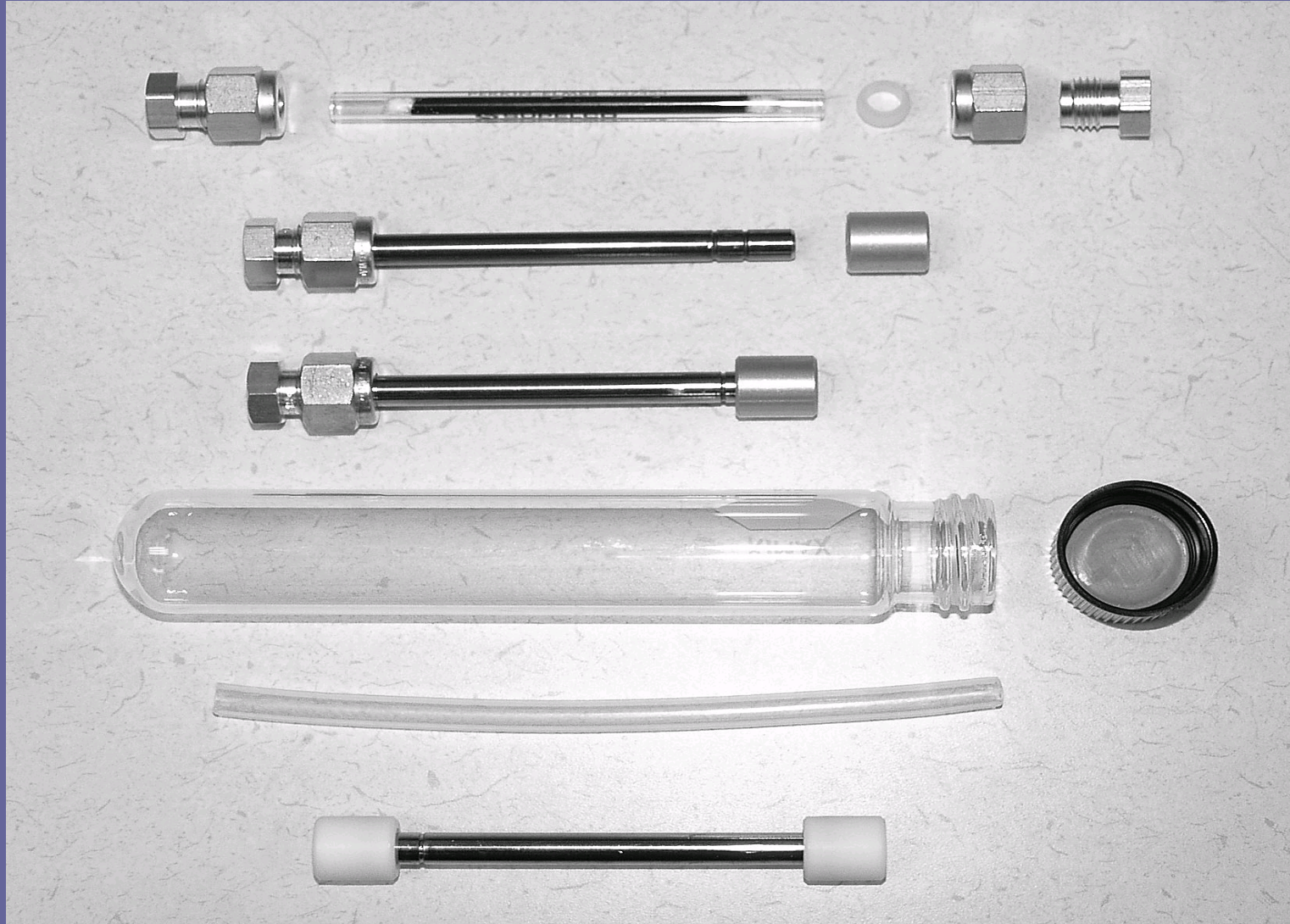
**The EPA/Monsanto Badge is a  
“Thin” Badge; the P.E./HSE  
Badge is a “Thick” Badge**



# DEARS Design of STB and Holder – Duplicate and Single Tube Badge

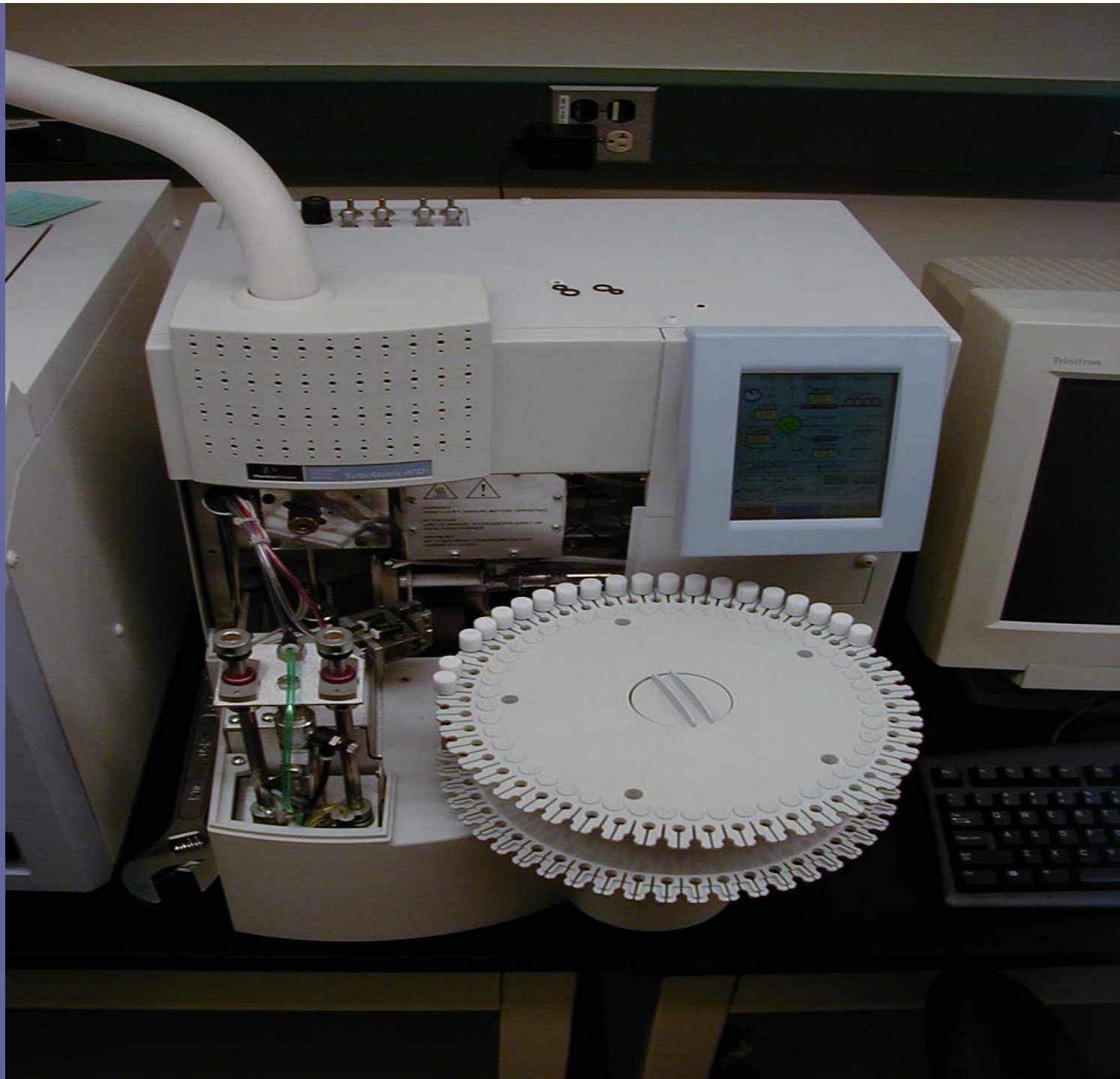


# Sampler Storage Accessories







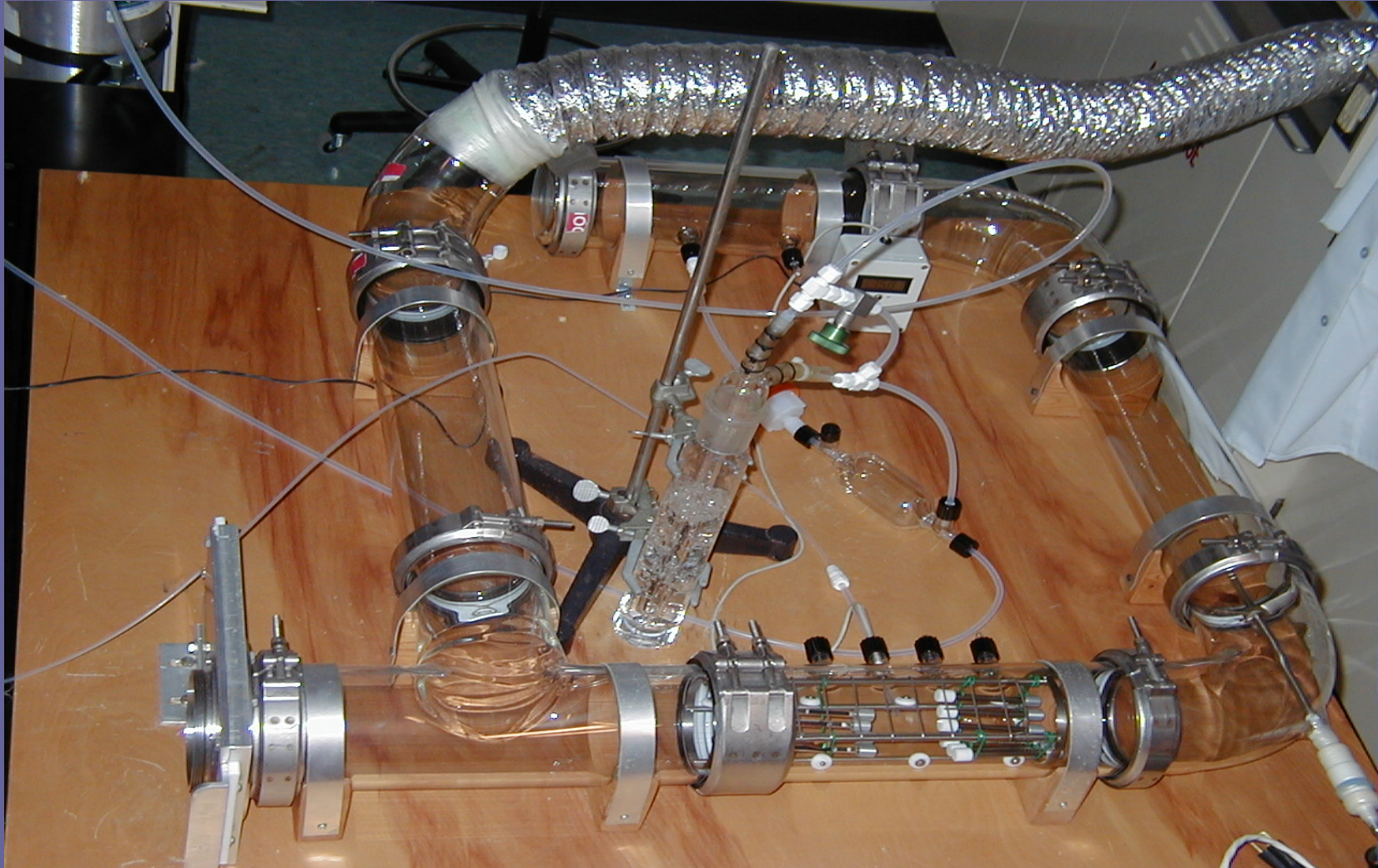








# Environmental Chamber for Testing Diffusive Samplers



## Ease of Use - QA Tradeoffs?

- **STBs are easy to handle, lightweight and small in size; no air pumps are used; for thermal desorption no solvents involved; cleaned for next use during thermal desorption; used many times; many compounds sampled; low cost.**

**But ...**

# QA Tradeoffs

- Sampling rate is compound dependent; sampling rate may be subject to change; tube-type samplers require opening, some assembly, and closure; calibration is more demanding; competition among VOCs for adsorption sites can cause problems; only a subset of VOCs can be sampled.

# Choice of Adsorbents – How to Estimate Adsorbent Capacity?

- Graphitic Carbons – Carbopack C, Carbopack X are examples.
- Carbopack X is microporous
- Desirable features include: high surface area; hydrophobicity
- Breakthrough Volume, Safe Sampling Volume

# Ideal and Non-Ideal Compound, Adsorbent Combination

The diffusive sampling equation:

$$dm/dt = (DA/L) * [C_a - C_o]$$

where m denotes target compound mass, D - diffusion coefficient, A - area, L - length,  $C_a$  - ambient concentration, and  $C_o$  gas phase concentration of target compound over the adsorbent.



# Ideal and Non-Ideal Diffusive Sampling Situations

- $C_o = 0$   
 $M = DAC_a T / L$
- $C_o \approx$  Amount of Material Adsorbed  
(Linear Isotherm) and sampling rate  
depends on concentration, time  
profile.

$$M = DAC_a T / L + DAC_o T/L$$

# Lot-to-Lot Variability in Commercial Samplers – Tube plus Adsorbent

- NERL/EPA recent experience with Carbopack X in Stainless Steel Tubes
- Testing for Lot-to-Lot Variability

# Testing under Different Conditions

- Reverse Diffusion – Loss from the Adsorbent in Non-Ideal Case
- Temperature and Humidity
- Response vs Concentration
- Presence of Other Compounds during Adsorption, Condensation of Water in Winter,

	11-25-2003 12 Hr + 12 Hr Reverse Diffusion	02-21-2004 1 Hr + 23 Hr Reverse Diffusion	12-05-2003 16 C vs 29 C Temperature	03-24-2004 35% vs 75% RH Humidity	02-13-2004 Time Varied Linearity
1,2-Dichloro-1,1,2,2-tetrafluoroethane	-12	-17	-8	6	0.999
1,3-Butadiene	-11	-22	-3	-12	0.998
Trichlorofluoromethane	0	14	-11	-2	0.999
1,1-Dichloroethene	-13	0	-10	-9	0.989
3-Chloropropene	-3	-16	-13	-17	0.977
1,1,2-Trichloro-1,2,2-trifluoroethane	-3	-2	-4	-2	0.999
1,1-Dichloroethane	-4	-7	5	12	0.996
cis-1,2-Dichloroethene	-5	-8	-1	-4	0.998
1,2-Dichloroethane	-3	-5	13	-3	0.988
1,1,1-Trichloroethane	1	8	-9	11	0.997
Benzene	-3	6	1	12	0.983
Carbon tetrachloride	2	7	-6	17	0.994
1,2-Dichloropropane	-1	1	13	-9	0.998
Trichloroethene	-3	16	1	7	0.998
1,1,2-Trichloroethane	7	-20	18	-9	0.977
Toluene	-2	1	-1	1	0.998
Tetrachloroethene	-2	1	5	1	0.998
Chlorobenzene	-3	1	2	-1	0.998
Ethylbenzene	-3	-1	0	-1	0.998
m,p-Xylene	-3	-3	2	-1	0.998
Styrene	-5	-2	2	-4	0.995
o-Xylene	-3	-2	4	-1	0.998
4-Ethyltoluene	-2	-15	9	-7	0.989
1,3,5-Trimethylbenzene	-4	-19	11	-4	0.995
	% Diff < 10%	% Diff < 20%	% Diff < 15%	RPD < 15%	R <sup>2</sup> > .990
	10% < % Diff < 20%	20% < % Diff < 30%	15% < % Diff < 20%	15% < RPD < 20%	.990 > R <sup>2</sup> > .975

# Consistency Checks

- Compare Active vs Diffusive Sampling.
- Compare Canister-Based Sampling vs Tube-Type Diffusion Sampling.
- What is Compliance with the Expectations during Field Deployment, i.e. following the SOPs for sampling, field blanks, etc.?

# Summary

- Try Tube-Type Diffusion Samplers for Ease of Use and Time-Integrated Samples  
- 24-Hours or Longer (4 weeks for some compound, adsorbent combinations).
- Test Commercial Lots to Insure that Materials Have Not Changed.
- Train Field Personnel in All Aspects of the Sampling SOP

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